OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT: N00014-93-1-0772

R & T Code 313T006

Technical Report #22

STUDIES OF THE KINETICS OF POLYOLMETHACRYLATE POLYMERIZATION BY FLUORESCENCE PROBES (PART III). POLYMERIC PHOTINITIATORS AND COINITIATORS.

Paczkowski, J.; Paczkowska, B.; Neckers, D.C. *Polimery-Tworzywa Wielkoczasteczkowe*, **1994**, *39*, 527-537, (1994).

D. C. Neckers
Center for Photochemical Sciences
Dept. of Chemistry
Bowling Green State University
Bowling Green, OHIO 43402

Date Submitted
June 15, 1995

REPORT DOCUMENTATION PAGE

OMB No. 0704-018

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	6-15-95	Technical Report

4. TITLE AND SUBTITLE
Studies of the Kinetics of Polyolmethacrylate Polymerization by Fluorescence Probes (Part III). Polymeric Initiators and Coinitiators

5. FUNDING NUMBERS
G N00014-93-J-1921
R & T 313T006

6. AUTHOR(S)
D.C. Neckers

Kenneth Wynne

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Center for Photochemical Sciences
Bowling Green State University
Bowling Green, Ohio 43402

8. PERFORMING ORGANIZATION REPORT NUMBER
22

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Navy
Office of Naval Research
800North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Paczkowski, J.; Paczkowska, B.; Neckers, D.C. *Polimery-Tworzywa Wielkoczasteczkowe*, 1994, *39*, 527-537, (1994).

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Changes in the fluorescence intensity and spectral characteristics of a fluorescent probe and FTIR spectroscopy have been used to follow the polymerization of polyolmethacrylates initiated by polymeric photoinitiators and a coinitiator. Polymerization photoinitiated by a polymeric photoinitiator forms a more rigid polymer and forms gels more rapidly than do monomeric initiator analogs. The use of varied sequences of initiating radiation supports the conclusion that the primary radicals formed during photoreduction of the visible photoinitiators are much less reactive in the case of the polymeric photoinitiator system. This causes a change from bimolecular termination to a unimolecular termination process. Fluorescence probe studies of the long-term postirradiation process were supplemented by FTIR studies which showed that the C=C conversion occurs before relaxation of free volume.

14. SUBJECT TERMS

15. NUMBER OF P.

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF
Unclassified	Unclassified	Unclassified	UL

STUDIES OF THE KINETICS OF POLYOLMETHACRYLATE POLYMERIZATION BY FLUORESCENCE PROBES (PART III). POLYMERIC PHOTINITIATORS AND COINITIATORS.

by

Jerzy Paczkowski[1], Bozena Paczkowska[1], D. C. Neckers*

Center for Photochemical Sciences[2]

Bowling Green State University

Bowling Green, OHIO 43403

ABSTRACT

Changes in the fluorescence intensity and spectral characteristics of a fluorescent probe and FTIR spectroscopy have been used to follow the polymerization of polyolmethacrylates initiated by polymeric photoinitiators and a coinitiator. Polymerization photoinitiated by a polymeric photoinitiator forms more a rigid polymer and forms gels more rapidly than do monomeric initiator analogs. The use of varied sequences of initiating radiation supports the conclusion that the primary radicals formed during photoreduction of the visible photoinitiators are much less reactive in the case of the polymeric photoinitiator system. This causes a change from bimolecular termination to a unimolecular termination process. Fluorescence probe studies of the long-term postirradiation process were supplemented by FTIR studies which showed that the C=C conversion occurs before relaxation of free volume.

BACKGROUND:

Polymeric sensitizers based on the xanthene dye Rose Bengal form the basis for most of what is known about heterogeneous sensitizers for photooxidation.[3] First examples were outlined in a 1973

A-1

paper[4] in which Rose Bengal was immobilized to chloromethylated polystyrene(co)divinylbenzene beads as a carboxylate ester. This notion was based on Merrifield's examples,[5] and has been reviewed.[6]

There are many known photopolymers which can be used to initiate polymerization in the UV region[7,8,9]. Among the examples are polymeric aromatic peresters[10] or polymeric derivatives of benzophenone[7]. There are no literature reports on polymeric photoinitiators which initiate polymerization by absorbing visible light. That is what we report in the present paper. We also report that major distinctions are observed in the polymerization of different polyolacrylate and polyolmethacrylate monomers when polymerization is initiated by polymeric initiators. Polymerization rates are followed by means of the fluorescence intensity and the spectral characteristics of a probe molecule present in the monomer mixture at the time of polymerization. Said probe follows microenvironment by both the wavelength and the intensity of its emission. These results have been supplemented by means of FTIR spectroscopy used to follow, in the steady state, double bond disappearance.

RESULTS AND DISCUSSION:

Certain rapid initiator systems for polyolacrylate polymerization at 514 nm (Argon ion laser; green line) are based on soluble derivatives of Rose Bengal which are derived by decarboxylation and conversion of the C-6 phenoxide to an ester[11]. An example is the acetyl deriviative of decarboxylated Rose Bengal which is generally used as a reductive photoinitiator with accelerators which may be, in the most successful cases, either triphenylalkyl borate esters[12] or, more practically, tertiary amines possessing α-hydrogens. The RBAX/tertiary amine initiator combination has the particularly intriguing capacity of bleaching at a rate essentially identical to the rate at which it initiates radical chains. Because RBAX absorbs over a range up to and including both the 488 nm and 514 nm lines of the argon ion laser, these two characteristics in combination allow one to initiate deep spikes of photopolymer at these wavelengths since the laser penetrates the monomer system at depth in the polymer forming events.

In prior work[13] the following mechanism for the photoreduction of the initiator, RBAX, in the presence of electron donors such as tertiary amines, (ED), has been established:

$$RBAX \longrightarrow RBAX(T) \qquad I_a f_T \qquad (3)$$

$$RBAX(T) \longrightarrow RBAX \qquad k_f \qquad (4)$$

$$RBAX(T) + ED \longrightarrow RBAX + ED \qquad k_1 \qquad (5)$$

$$RBAX(T) + ED \longrightarrow \{RBAX^{\cdot -} ED^{\cdot +}\} \qquad k_2 \qquad (6)$$

$$\{RBAX^{\cdot -} ED^{\cdot +}\} \longrightarrow \text{bleaching products} \qquad k_3 \qquad (7)$$

$$\{RBAX^{\cdot -} ED^{\cdot +}\} \longrightarrow RBAX^{\cdot -} + ED^{\cdot +} \qquad k_4 \qquad (8)$$

The polymerization step proceeds according to reactions (9-12):

$$RBAX^{\cdot -} \longrightarrow RB + Ac^{\cdot} \qquad k_5 \qquad (9)$$

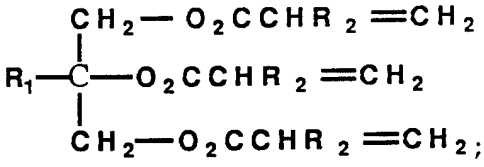
$$ED^{\cdot +} \longrightarrow ED^{\cdot} + HA \qquad k_6 \qquad (10)$$

$$ED^{\cdot} + M \longrightarrow M_1^{\cdot} + M \longrightarrow M_2^{\cdot} + \cdots + M \longrightarrow M_n^{\cdot} \quad \text{polymerization and propagation} \qquad (11)$$

$$M_n^{\cdot} + ED^{\cdot} \text{ (or } Ac^{\cdot} \text{ or } M_m^{\cdot}) \longrightarrow \text{inert polymer} \quad \text{termination} \qquad (12)$$

Bleached products have been isolated in model systems[14,15,16] and derive from (7) and from the reaction of $RBAX^{-\cdot}$ with H^+. The radical Ac· released by $RBAX^{-\cdot}$ (9) has been proposed to terminate radical chains, rather than initiate them based on a square root relationship of polymerization rate to light intensity.

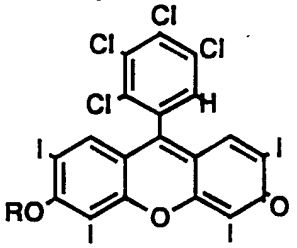
It is already known that (i) photoinitiated polymerizations of highly functionalized monomers such as TMPTA and TMPTMA (1)



$R_1 = CH_3$, R_2 =H; (1),

generally exhibit non-conventional kinetic behavior in that the polymerization rate is dependent on the conversion degree[17], (ii) the induction period for the onset of polymerization is affected by the presence of oxygen[18], (iii) the degree of polymerization and the quantum yield of photoinitiated polymerization is affected by the manner of irradiation[19,20,21] and (iv) polymerization is accompanied by heat evolution, free volume relaxation, rheological changes[22,23,24,25] and by monomer diffusion into polymer matrix[26]. Though kinetic analysis of polymer mixtures rapidly transforming from the liquid phase into a solid gel[27,28] is complicated, several methods have already been used to study this process. The most accurate of these is a method devised by Decker which employs real-time infrared spectroscopy [RTIR] to follow the rate of polymerization by recording the double bond conversion of monomer[25,29,30]. Though Decker's method is only applicable to thin films, it allows one to calculate the quantum yield of double bond conversion, the kinetic chain length of polymerization or to describe the kinetics of the dark reaction; i. e., the chemical reaction after initiation is ceased. Decker's method fails to provide information on the actual polymerization process i. e., what is occurring to the three dimensional shape and configuration of the forming matrix during the formation of the macromolecular network. It is for this reason, and for others, that we have developed fluorescence probe methodology to follow polymerization rates of highly functionalized monomers in real time.[22,31,32,33]

The properties of the photoinitiators used are described in Table I. Monomeric photoinitiators used in this work were decarboxylated Rose Bengal and its acetylated derviative (2), Table I:



R = H {RBOH}; R = Ac{RBAX} (2)

Polymeric analogs were derived by reaction of RBOH with acryloyl chloride followed by polymerization (Poly RBAX; Part I; Table I), and from Poly(methacryloyl chloride); (Poly RBAX; Part II; Table I). Polymer Rose Bengal[34] was acidifed (Poly RBOH; Table I) and that product acetylated (Poly RB-OAc: Table I). The structures of these polymers are shown in Scheme I.

Scheme I

Table I

The Photoinitiators

Initiator	$\varepsilon_{514\,nm}$	MW	MW of the color unit
RBAX	7000	970	970
RBOH	7000	928	928
Poly-RBAX	part I ——	90,000	12,950
	part II ——	mixture	1,295
Poly-RBOH	——	55,000-60,000	2,865
Poly-RB-OAc	——	55,000-60,000	2,865

Figure 1 shows the changes of fluorescence intensity of dansyl amide (hereafter DA) observed at 460 nm and 500 nm during the photoinitiated polymerization of TMPTA.

Figure 1

Polymerization was initiated by a series of argon ion laser (514 nm) flashes[35] (large relay sequence (LRS), time of single flash 200 ms, 15 flashes) using the initiator system RBAX, ($c=5x10^{-4}$ mol/l) and N-phenyl glycine (NPG, c=0.05 mol/l). Polymerization causes a decrease in the available free volume and this, in turn, affects the microenvironment of the probe causing an increase in probe fluorescence.

The ratio of fluorescence intensities of the probe at multiple wavelengths indicate the degree of polymerization. At least two other things may account for a sharp increase in probe fluorescence intensity. During the irradiation RBAX bleaches[13] (Φ=0.132). Since RBAX also quenches the fluorescence of DA, a decrease in RBAX will cause an increase in the observed fluorescence intensity of the probe. A second reason to which a fluorescence intensity increase might be attributed is related to the heat evolved during the polymerization of acrylates. Thermal changes affect the fluorescence intensity at both wavelengths.

Figure 2a shows the changes of the fluorescence intensities (at 460 nm and 500 nm) observed during and after pulsed irradiation of a visible system (RBAX;c=11×10^{-4} mol/l and NPG;c=0.05 mol/l) with TMPTMA.[36]

Figure 2a,b,c

There are significant differences in the polymerization responses of the probe in TMPTA (Fig. 1) and TMPTMA (Fig. 2a). For TMPTA, even after the first flash (200 ms), one observes an increase in the fluorescence intensity. The observed fluorescence intensity remains stable, and changes caused by diffusion of the initiator or monomer into the observation area are not observed. Changes in the fluorescence intensity of the probe observed after irradiation of the mixture containing TMPTMA are more complex. After each flash a sharp increase of fluorescence is observed followed by a decrease in fluorescence resulting, we postulate, from the diffusion of RBAX into the observation area. Even after 15 flashes (total time of irradiation 3 sec.) one sees no formation of a solid polymeric spike under the conditions (laser power, initiator concentration, coinitiator concentration) though dramatic changes of fluorescence intensity of the probe molecule are observed. For RBAX concentrations as high as 1.1×10^{-3} mol/l no poly(TMPTMA) can be detected via GPC. In comparison when a similar large relay sequence (LRS) of irradiations as for the TMPTMA was performed on a mixture which contained RBAX but no NPG (see Figure 2b), the changes in probe responses are identical for both experiments. This confirms no apparent polymerization is occurring in the former case. We conclude that during irradiation the concentration of the primary free radicals must be high enough to cause direct termination; in

photographic terms, *reversal*. In the instance of TMPTMA the rate of termination of the primary radicals is much higher than the rate of polymerization.

$$k_p[M][R^{\cdot}] < k_T[R^{\cdot}]^2 \qquad (14)$$

As further evidence for this, we have decreased the concentration of the initiator; in effect reducing radical concentrations. Under these circumstances the formation of solid polymer is apparent. The kinetic fluorescence traces of one such system is shown in Figure 2c. As polymerization of the monomer progresses, the viscosity of the mixture increases, and this slows down all processes that depend on diffusion. As indicated above we have previously observed that many tertiary aromatic amines[37] are highly efficient as electron donors in the photoreduction of RBAX. Thus we synthesized and tested three polymeric coinitiators; Poly N,N-dimethylaminobenzoate (Poly-DAB); Poly N,N-dimethylaminocinnamate (Poly-BDAC);[38] and polymer immobilized N-phenylglycine (Poly-PG). Their structures are shown in Scheme II, and their properties in Table II.

Scheme II

Table II

Polymeric Coinitiators

coinitiator		MW	MW of ED unit*
Poly-PG	——	40,000	——
Poly-DAB	——	55,000-60,000	616
Poly-BDAC	——	55,000-60,000	590

* Molecular weight of electron donating unit (coinitiator unit).

Figure 3 shows the probe response observed during and after irradiation of a TMPTMA-VP mixture containing RBAX ($c=11x10^{-4}$ mol/l) and Poly-PG (concentration of electron donating groups 0.05 mol/l). One recalls, Figure 2a, that for an RBAX concentration as high as $1.1x10^{-3}$ mol/l and using NPG as a coinitiator, the termination process of the primary radicals was

Figure 3

much faster than the chain initiating process and no polymer is formed. From the data, Fig. 3, one concludes that in the case of the polymeric coinitiator, Poly-PG, under the same initiating conditions, a semi-rigid polymeric bar is formed after the first 200 ms flash. As the series of flashes proceeds, more RBAX is bleached in the irradiation area and the overall fluorescence intensity increases. The polymer becomes more rigid, however, and smaller changes in the fluorescence intensity occur between flashes. After irradiation the fluorescence of the probe slowly decreases due to the diffusion of monomer/initiator mixture into polymeric bar from the nonpolymerized environment. The rate of monomer diffusion into the polymerized bar is relatively high and it changes on the time scale of minutes. Such a fast process is possible only when the crosslink density is low, and the system is more gel-like than like a highly crosslinked polymer[39]. The termination process in which two macroradicals must diffuse towards each other is more strongly affected by increasing solution viscosity than is the propagation reaction in which one of the partners is the mobile free monomer. The polymeric coinitiator, after photoreaction with RBAX, forms a macroradical and this decreases the termination rate of the primary radicals as well as the termination rate of the macroradicals. Since the polymerization process starts on the macroradical, the formed polymer is highly branched from the outset with the degree of crosslinking controlled by the rate of termination. Poly-DAB and Poly-BDAC behave similarly to Poly-PG.

We have mentioned earlier that the rate termination of macromolecular radicals is strongly influenced by increasing solution viscosity. Considering the mechanism of radical formation from RBAX, one concludes that from Poly-RBAX one should obtain a macroradical whose terminating rate is

strongly affected by the viscosity of the polymerized system. In other words the rate of termination might be much lower for polymerization initiated by the polymeric initiator. Figure 4 shows the fluorescence intensity change during the photoinitiated polymerization of TMPTMA-VP by Poly-RBAX in which NPG is used as the coinitiator. The ratio of fluorescence intensities indicates that after 3 sec of irradiation the degree of monomer conversion into polymer is not high. However since the

Figure 4

fluorescence intensity ratio (I(460)/I(500)) is increasing it is suggested that polymerization remains in progress. Were this so, the manner in which the irradiation is carried out could influence the final degree of monomer conversion into a polymer.

Figure 5 shows the data obtained for photoinitiated polymerization of TMPTMA-VP by Poly-RBAX using various forms of irradiation. Similar total times of irradiation were obtained by employing one single flash, or by using two, three, four or more flashes of shorter duration in sequence. The results indicate that polymerization continues after irradiation, and that the continuing irradiation causes a faster termination of the macroradicals. The latter is caused by formation of primary radicals which initiate a large number of chain reactions which are terminated at low molecular weight. Based on this result, one might anticipate that the time separating flashes of irradiation may influence the total degree of monomer conversion into a polymer.

Figure 5

This is confirmed by the data in Figure 6. In these experiments the photoinitiated polymerization of a TMPTMA-VP mixture by Poly-RBAX using various large relay sequences is reported. The results are not surprising for LRSs with a short pause between flashes[16,40] since, in each case, the radicals generated by the next flash are able to initiate a new generation of polymer radicals as well as terminate the living polymer chains initiated by earlier flashes.

Figure 6

A more interesting situation is observed if one employs longer separations between the flashes. One can see that even for pauses longer than 10 sec, a change in the ratio of fluorescence intensities continues. In order to confirm whether polymerization is continuing when Poly-RBAX is used as the photoinitiator, an identical polymerization experiment was carried out, but the polymerization progress was followed using FTIR spectroscopy. These results are presented in Figure 7. The degree of double bond conversion of methacrylate strongly depends on the time of the pause between laser flashes.

Figure 7

The data obtained for RBAX (or low molecular weight Poly-RBAX, which based on GPC measurements, contains RBAX) shows (both Fig. 6 and Fig. 7) that the final degree of polymerization essentially is independent on the manner of irradiation when low molecular weight initiators are used. But for high molecular weight Poly-RBAX, there is a pronounced effect of the irradiation sequence and the time on the final degree of polymerization. Using a proper LRS, one can reach at least twice the degree of double bond conversion one is able to obtain with RBAX. We surmise the effect of initiator structure on degree of polymerization is the result of the size of the primary terminating radicals formed in photoreduction of the photoinitiators. RBAX forms a mobile acetyl radical, while Poly-RBAX forms a macroradical. The termination rate of the macroradical is strongly influenced by diffusion and the autoacceleration effect of the polymerization is more significant. One more interesting feature of both initiators (monomeric and polymeric) should be pointed out. Figures 8 and 9 show how long after irradiation polymerization continues. Surprisingly, the rate of long-term polymerization is almost identical for both photoinitiators.

Figure 8

Figure 9

This behavior is explained by assuming that macroradicals are trapped in a polymeric network[21,41,42]. Fitting the curves describes the following equation:

$$\% \text{ of double bond conversion} = at^b \qquad (15)$$

where: t = time and a, b constants. The b values obtained (Fig. 9) are 0.168 for the polymerization photoinitiated by RBAX, and 0.148 for the polymerization photoinitiated by Poly-RBAX. This strongly suggests that similar kinetics pertain in the long-term post-irradiation polymerization driven by both photoinitiators. The fitting performed for the data obtained using the fluorescence probe method gives b=0.039 in both instances. *The obvious conclusion is that for the long-term post-irradiation processes, C = C conversion occurs more rapidly than does free volume relaxation*[42].

The difference between Poly-RBAX and RBAX appears on the tens of seconds time scale. This results, we suggest, from the high mobility of acetyl radicals and the low mobility of the macroradicals formed from poly-RBAX. The typical steady state treatment of such a photoinduced polymerization gives the following equation to describe the rate of polymerization;

$$-d[M]/dt = k_p(I_a/k_t)^{0.5}[M] \qquad (16)$$

where [M] = concentration of monomer, I_a = intensity of light, k_p and k_t are the rate constants of the polymerization and the termination processes. The rate of polymerization described by eq. 16 results from the assumption that both types of radicals e.g., the acetyl radical and the macroradical, exhibit the same rate of chain termination. However, the results presented in Figures 6 and 7 show that the kinetics of the termination process are more complex when one uses the polymeric photoinitiator. A mechanism of polymerization and termination consistent with these observations is:

Radical formation;

$$\text{Poly-RBAX}^{\cdot} \longrightarrow \text{RB} + \text{Poly-MM}^{\cdot} \qquad (17)$$

Polymerization as described by eq. 10 and eq. 11.

and the termination steps are:

$$M_n^{\cdot} + ED^{\cdot} \longrightarrow \text{inert polymer} \qquad k_7 \qquad (18)$$

$$M_n^{\cdot} + \text{Poly-MM}^{\cdot} \longrightarrow \text{inert polymer} \qquad k_8 \qquad (19)$$

$$M_n^{\cdot} + M_n^{\cdot} \longrightarrow \text{inert polymer} \qquad k_9 \qquad (20)$$

There is also a termination which involves the primary radicals:

$$ED^{\cdot} + \text{Poly-MM}^{\cdot} \longrightarrow \text{inert polymer} \qquad k_{10} \qquad (21)$$

The rates of the processes described by equations 18, 19 and 21 are low when compared with the rate of the process described by eq. 20. Otherwise polymerization would not proceed. Thus the final equation which describes the rate of termination (Equation 22) describes a unimolecular termination process:

$$-d[R^{\cdot}]/dt = k_9[M_n^{\cdot}] \approx k_9[ED^{\cdot}] \qquad (22)$$

Using the steady-state approximation;

$$[ED^{\cdot}] = I_a\Phi_T/k_t \qquad (23)$$

The final equation describing the rate of polymerization photoinitiated by the Poly-RBAX and NPG initiating system is:

$$-d[M]/dt = (k_p/k_t)\, I_a\Phi_T[M] \qquad (24)$$

If the kinetic scheme represented by equations 18 - 21 is correct, a measurement of the rate of polymerization obtained by measuring of the weight of the isolated polymeric spikes (obtained by irradiation of a small fraction of total monomer volume with the time of single flash of 100 ms), should be first order with respect to the light intensity. This is because the time of a single flash used for the spike formation (100 ms) is much shorter than the postirradiation processes observed to be on the time scale of seconds. The measurements are presented in Figure 10 and confirm the proposed first order dependence.

Figure 10

One can conclude that for polymerization initiated by a polymeric photoinititor irradiated using short flashes, only a unimolecular termination process involving only one type of radical is involved. In contrast, for RBAX, the rate of polymerization varies with the square root of the laser intensity. This confirms the presence of two different types of terminating radicals[13].

Two other polymeric photoinitiators, e.g. Poly-RBOH and Poly-RB-OAc were tested using both the FTIR and fluorescence probe techniques. The fluorescence probe response observed during the polymerization of a TMPTMA-VP mixture photoinitiated by Poly-RBOH with NPG as a coinitiator is recorded in Figure 11. Figures 12 A, B, show data obtained for the photopolymerization initiated by Poly-RB-OAc.

Figure 11

Figure 12 A, B

The recorded changes for the photoinitiated polymerization are more pronounced for both polystyrene initiators than are those observed when polymerization is photoinitiated by Poly-RBAX. In both cases, polymerization continues for a substantial time after irradiation, and the final degree of polymerization depends on the irradiation process. Figure 13 shows the relationship between the time of the pauses separating the flashes and the final ratio of fluorescence intensities reached after the temperature equilibrates to room temperature. A higher ratio of fluorescence intensities is observed for those cases in which there is a longer pause between flashes. Similar experiments with varying LRSs were carried out using the FTIR technique to measure double bond conversion, Figure 14. Poly-RB-OAc and Poly-RBAX behave similarly. This is surprising because, according to the kinetic scheme described (3 - 10), the photoreduction of Poly-RB-OAc should form an acetyl radical, and we already know this acts as a chain terminator. The unusual behavior of Poly-RB-OAc is confirmed by the data presented in Figure 10. The results indicate that for the polymerization initiated by Poly-RB-OAc there is also a unimolecular termination process in which acetyl radicals are not involved in terminating the chain. There are three possible explanations for this behavior. One is that the acetyl radical formed

abstracts hydrogen from the proximate polystyrene chain. The second is that the radical anion of the Rose Bengal molecule abstracts the hydrogen from the proximate polystyrene chain, and this prevents formation of acetyl radical. Or photoreduction of the undecarboxylated Rose Bengal produces a different radical anion than that formed from the decarboxylated Rose Bengal system. This is not regarded likely. There is no direct evidence indicating which mechanism is correct. However all of the processes form a macroradical which has a low rate of termination in a mechanism analogous to that proposed for Poly-RBAX. The only difference is the locus of the radical center.

Figure 13

Figure 14

The post irradiation behavior of the polymerized system is similar to that observed for Poly-RBAX. This is illustrated by the FTIR measurements of double bond conversion (see Figure 15) which are observed to be on the time scale of tens of minutes.

Figure 15

In conclusion, the kinetics of the polymerization photoinitiated by monomeric and polymeric initiators are quite different. The use of varied irradiation sequences allows one to conclude that the primary radicals formed during photoreduction of a visible photoinitiator are much less reactive as terminating radicals when the system involves a polymeric photoinitiator than they are when they result from monomeric photoinitiators. Thus bimolecular chain termination in the former case becomes a unimolecular termination process in the latter. The experimental data show that the use of polymeric initiators and coinitiators cause two different chemical amplification effects: the first is the photoinitiated chain polymerization with possibility of control of termination process. The second is the crosslinking process from the polymer chain existing in starting material as a polymeric initiator and coinitiator. The measurements performed for the long-term postirradiation process were supplemented by FTIR spectroscopy which showed that the C=C conversion runs ahead of the free volume relaxation.

EXPERIMENTAL

General

Decarboxylated Rose Bengal, neutral form (RBOH) and acetylated decarboxylated Rose Bengal (RBAX) were prepared using procedures described earlier[13]. 1,1,1-Trimethylolpropane triacrylate (TMPTA), and 1,1,1-trimethylolpropane trimethacrylate (TMPTMA), were purchased from Sartomer and used without purification. 1-Vinyl-2-pyrrolidinone (VP), N-phenylglycine (NPG), dansyl amide (DA) and 4-methylstyrene were purchased from Aldrich. Poly(methacryloyl chloride) and methacryloyl chloride were obtained from Polysciences and chloromethylstyrene from TCI. All of these compounds, with the exception of chloromethylstyrene, were used without further purification.

Measurements were carried out using solutions composed of 1 ml of VP, 9 ml of the appropriate multifunctionalized acrylate or methacrylate, a Rose Bengal derivative either monomeric or polymeric as the photoinitiator with an effective concentration of dye $\approx 10^{-4}$ M, and monomeric or polymeric coinitiators the concentration of which was c=0.05 mol/l. Dansyl amide, the probe molecule, was present at the concentration of $c=5.24\times10^{-4}$ mol/l.

Real-time kinetics of the polymerization were carried out using the apparatus described elsewhere[22]. FTIR measurements were performed using a 6020 Galaxy Series FT-IR spectrophometer.

Soluble Polymer bound 6-O-Acetylated Rose Bengal (Poly-C(O)O-RB-OAc).

2.0 g of Poly-C(O)O-RB-OH [31] was dissolved in 25 ml of $CHCl_3$. To the solution 2 ml of pyridine was added. The orange solution turned red. The solution was stirred while 2 ml of acetyl chloride was added dropwise. The mixture was stirred for an additional hour. The red solution turned orange once again. The final product was precipitated with an excess of methanol and purified by repeated precipitation from $CHCl_3$ with excess of methanol. Analytical data: molecular weight of the color unit: 2865, molecular weight of starting chloromethylated polystyrene: 55,000-60,000; the shape and the position of the electronic absorption maxima of the dye is similar in the polymeric product to that observed for RBAX.

Copoly(-6-O-Rose Bengal methacrylate-methyl methacrylate) (Poly-RBAX)

Method I

Decarboxylated Rose Bengal (neutral form) 1.85g was dissolved in 25 ml of $CHCl_3$ and 2 ml of pyridine was added. The solution turned red. To the stirred solution 2 ml of methacryloyl chloride was added dropwise. Stirring was continued for an additional hour during which time the solution turned back to the orange. The product was precipitated in methanol, filtered and dried. The structure of the product, 6-O-Rose Bengal methacrylate (RB-OMM) was confirmed using IR and NMR spectroscopy.

Copolymerization of 6-O-Rose Bengal methacrylate (RB-OMM) and methyl methacrylate.

RB-OMM (2.0g) and AIBN (1.44g) were dissolved in 20 ml of methyl methacrylate. Polymerization was carried out in glass tubes by heating at 50^{o} for 24 hours. The resulting copolymer was dissolved in chloroform, precipitated with methanol, and the product purified by repeated precipitation in methanol. Analytical data: molecular weight of the color unit: 12,950, polymer MW (GPC): 90,000; the shape and position of the electronic absorption maxima are similar to that observed for RBAX.

Method II

Decarboxylated Rose Bengal, neutral form (RB-OH), (1.85g) was dissolved in 25 ml of dioxane. To the stirred solution 5 ml of pyridine was added, and 5 g of poly(methacryloyl chloride) in dioxane (Polysciences) was added dropwise. The orange mixture was stirred for 2 hours, then 5 ml of methanol was added and stirring was continued for additional 1 hour. The product was precipitated with methanol and purified by repeated precipitation from $CHCl_3$. Analytical data: molecular weight of color unit: 1,295. GPC analysis indicates presence of high molecular weight (about 80,000) and low (close to RB-OMM) molecular weight components; the shape and the position of the electronic absorption maxima are similar to that observed for RBAX.

SOLUBLE POLYMER BOND COINITIATORS

Soluble polymer bound N-phenylglycine; copoly{styrene-N-phenyl-N-(vinylbenzyl)glycine}; (Poly-PG)

Bromomethylated polystyrene (4.03g;10 mmol of -CH_2Br groups) and 1.8 g (12 mmol) of N-phenylglycine were dissolved in 25 ml of DMF. The solution was stirred for 24 hours at 60°C, and the resulting product precipitated by an excess of methanol and purified by repeated precipitation from $CHCl_3$. Analytical data: MW (GPC): 40,000; The monomeric equivalent of Poly-PG was prepared by reaction of a unimolar mixture of N-phenylglycine and benzyl bromide under identical conditions to those used for Poly-PG preparation. The product was precipitated in MeOH-H_2O (1:1) mixture and crystallized from methanol. Yield: 82 %; NMR (^1H) ($CDCl_3$); ppm: 4.126 (s, 2H, -CH_2COOH), 4.645 (s, 2H, CH_2-Ph), 6.698-7.341 (m, 10 H, phenyl); product: N-phenyl-N-benzylglycine.

Soluble polymer bound N,N(4-dimethylamino)benzoate; copoly{styrene-4-vinylbenzyl N,N(4-dimethylamino)benzoate}; (Poly-DAB)

Chloromethylated polystyrene 4.64 g (10 mmol of -CH_2Cl groups) was dissolved in 30 ml of DMF. To the solution 2.23 g (12 mmol) of potassium N,N(4-dimethylamino)benzoate and 0.5 g of tetrabutylammonium bromide which served as a catalyst were added. The mixture was stirred for 24 hours at ambient temperature. The product was precipitated in methanol and purified by repeated precipitation. Analytical data: MW (GPC): 55,000-60,000. The monomeric equivalent of Poly-DAB was prepared by reaction of a unimolar mixture of potassium N,N-(4-dimethylamino)benzoate and benzyl chloride under conditions similar to those used in the case of Poly-DAB. The product was precipitated with a MeOH-H_2O (1:1) mixture and crystallized from methanol. Yield: 76%; NMR (^1H)($CDCl_3$); ppm: 3.063 (s, 6H, -$N(Me)_2$), 5.330 (s, 2H, Ph-CH_2-OC(O)), 6.887,6.930 (J_{AB}=8.6 Hz, 2H, 1,4 substituted phenyl), 7.341-7.414 (m, 5H, phenyl), 7.983, 8.026 (J_{AB}=8.6 Hz, 2H, 1,4 substituted phenyl).

Soluble polymer bond N,N(4-dimethylamino)cinnamate; copoly{styrene-4(3)vinylbenzyl N,N(4-dimethylamino)cinnamate};(poly-BDAC)

Poly-BDAC was prepared using the same procedure as for Poly-DAB. Analytical data: MW (GPC): 55,000-60,000. Monomeric equivalent: NMR (^1H) ($CDCl_3$); ppm: 3.008 (s, 6H, $-N(Me)_2$), 5.250 (s, 2H, Ph-CH_2-OC(O)), 6.252, 6.332 (J_{AB}=16 Hz, 1H), 6.848, 6.692 (J_{AB}=8.8 Hz, 2H, phenyl cinn.), 7.390-7.447 (m, 7H, phenyl cinn. and benzyl), 7.653,7.733 (J_{AB}=16Hz, 1H).

ACKNOWLEDGMENT

This work has been supported by the National Science Foundation (DMR 9013109). We are most grateful for this support. We also acknowledge many helpful discussions with Jon Arney, Oscar Valdes-Aguilera and George S. Hammond.

REFERENCES

---

[1]On leave from the Department of Chemistry and Chemical Engineering, Technical and Agricultural University, Seminaryjna 3, 85-326 Bydgoszcz, Poland

[2]Contribution # from the Center for Photochemical Sciences

[3]Paczkowski, J. and Neckers, D. C., *Macromolecules*, **1985**, *18*, 1245.

[4]Blossey, E. C., Neckers, D. C., Thayer, A. L., Schaap, A. P., *J. Amer. Chem. Soc.*, **1973**, *95*, 5820.

[5]Merrifield, R. B., *J. Amer. Chem. Soc.*, **1963**, *85*, 2149.

[6]Neckers, D. C., *Reactive Polymers*, **1985**, *3*, 277.

[7]Gupta, N. S., Thijs, L., Neckers, D. C., *Macromolecules*, **1980**, *13*, 1037.

[8]Gupta, I., Gupta, N. S., Neckers, D. C., *J. Polym. Sci.: Polym. Chem. Ed.*, **1982**, *20*, 147.

[9]Gupta, S. N., Thijs, L., Neckers, D. C., *J. Polym. Sci.: Polym. Chem. Ed.*, **1981**, *19*, 855.

[10]Gupta, N. S., Gupta, I., Neckers, D. C., *J. Polym. Sci.: Polym. Chem. Ed.*, **1981**, *19*, 103.

[11]Neckers, D. C., "Production of Three Dimensional Bodies by Photopolymerization", U.S. Patent #5,137,800 (August 11, 1992).

[12]Chatterjee, S., Gottschalk, P., Davis, P. D., Schuster, G. B., *J. Amer. Chem. Soc.*, **1988**, *110*, 2326.

[13]Valdes-Aguilera, O., Pathak, C. P., Watson, D., Shi, J., and Neckers, D. C., *Macromolecules*, **1992**, *25*, 541.

[14]Zakrzewski, A., and Neckers, D. C., *Tetrahedron*, **1987**, 43, 4507.

[15]Shi, J., Zhang, X., Neckers, D. C. *J. Org. Chem.*, **199257**, 4418.

[16]Shi, J., Zhang, X., Neckers, D. C. , *Tet. Letters*, **1993**,34 ,6013

[17]Timpe, H. J., Strehmel, B., *Makromol. Chem.*, **1991**, *192*, 779.

[18]Decker, C., Moussa, K., *Macromolecules*, **1989**, 22, 4455.

[19]Decker, C., Moussa, K., *Makromol. Chem.*, **1990**, *191*, 963.

[20]Hoyle, C. E., Trapp, M. A., Chang, C. H., Lantham, D. D., McLaughlin, K. W., *Macromolecules*, **1989**, 22, 3866.

[21]Hoyle, C., Trapp, M. A., *J. Imaging Sci.*, **1989**, *33*, 188.

[22]Paczkowski, J., Neckers, D. C., *Chemtracts,, Macromolecules Edition*, **1992**, *3*, 75.

[23]Bowman, C. N., Peppas, N. A., *Macromolecules*, **1991**, 24, 1914.

[24]Macosko, C. W., *British Polym. J.*, **1985**, *17*, 239.

[25]Kloosterboer, J. G., van de Hei, G. M. M., Gossik, R. G., Dorant, G. C. M., *Polymer Comm.*, **1984**, *25*, 322.

[26]Krongauz, V. V., Yohannan, R. M., *Polymer*, **1990**, *31*, 1130.

[27]Decker, C., Moussa, K., *ACS Symposium Series*, **1990**, *417*, ch. 31, 439.

[28]Anseth, K. S., Wang, C. M., Bowman, C. N., *Macromolecules*, **1994**, *27*, 650.

[29]Decker, C., Moussa, K., *Makromol Chem.*, **1988**, *189*, 2381.

[30]Decker, C., *Macromolecules*, **1990**, *23*, 5217.

[31]Neckers, D. C., Paczkowski, J., *Macromolecules*, **1991** 24, 3013.

[32]Zhang, X., Kotchetov, I.N.,Paczkowski, J., Neckers, D.C. , *J. Imag. Sci.*, **199236**, 4, .

[33]Neckers,D.C. , Paczkowski, J., *J. Poly. Sci. A, Chem.*, **199331**, 841.

[34]Synthesis see: Paczkowska, B., Paczkowski, J., Neckers, D.C., *Macromolecules*, **1986**, *19*, 863.

[35]We use this terminology to distinguish using a CW laser for a short irradiation time from using a pulsed laser.

[36]Moore, J. E., "UV Curing: Science and Technology", Technology Marketing Corporation; **1978**, 134.

[37]Postlewaite, J. J., Valdes-Aguilera, O., Paczkowski, J., Neckers, D. C. - unpublished data.

[38]Paczkowski, J., Toczek, M., Scigalski, F., Cwiklinska, D., Sierocka, M., *J. Polym. Sci. Part A: Polym. Chem.*, **1989**, *27*, 2647.

[39]The use of Poly-PG as a coinitiator for polymerization of TMPTA decreases the rate of polymerization. This may be due to structural differences between NPG and Poly-PG. NPG is the secondary amine, while in Poly-PG phenylglycine molecule is a tertiary amine (see experimental section).

[40]Haldcroft, S., Guillet, J. E., *J. Polym. Sci.; Part A: Polym. Chem.*, **1991**, *29*, 729.

[41]Bellbono, I. G., Oliva, C., Morelli, R., Selli, E. E., Ponti, A., *J. Chem. Soc. Faraday Trans.*, **1990**, *86*, 3273.

[42]Kloosterboer, J. G., Lijten, G. F. F. M., Greidanus, F. J. A. M., *Polymer Comm.*, **1986**, *27*, 268.

Figures:

Fig. 1 The change of dansyl amide fluorescence recorded after the polymerization of a TMPTA-VP (9:1) mixture: RBAX ($10x10^{-4}$ mol/l), NPG (0.05 mol/l), LRS (0.2-10-....), 15 flashes, total time of irradiation 3 sec., 600 mW/1.54 mm^2, 514 nm.

Fig. 2 The changes of dansyl amide fluorescence recorded during and after photoinduced polymerization of a TMPTMA-VP (9:1) mixture:

a) RBAX ($11x10^{-4}$ mol/j), NPG (0.05 mol/l), LRS (0.2-10-.....), 15 flashes, 600 mW/1,54 mm^2, 514 nm.

b) RBAX ($5x10^{-4}$ mol/l), NPG (0.000 mol/l), LRS (0.2-10-.....), 15 flashes, 600 mW/1.54 mm^2, 514 nm.

c) RBAX ($5x10^{-4}$ mol/l), NPG (0.05 mol/l), LRS (0.2-10-.....), 15 flashes, 600 mW/1.54 mm^2, 514 nm.

Fig. 3 The changes of dansyl amide fluorescence recorded during and after polymerization of a TMPTMA-VP (9:1) mixture: RBAX ($11x10^{-4}$ mol/l), Poly-PG (0.05 mol/l of PG molecules), LRS (0.2-10-....), 15 flashes, total time of irradiation 3 sec., 600 mW/1.54 mm^2, 514 nm.

Fig. 4 The changes of dansyl amide fluorescence recorded during and after polymerization of a TMPTMA-VP (9:1) mixture: Poly-RBAX ($5x10^{-4}$ mol/l of RB), NPG (0.05 mol/l), LRS, (0.2-10-...), 15 flashes, total time of irradiation 3 sec., 600 mW/1.54 mm^2, 514 nm.

Fig. 5 The effect of different methods of irradiation on the final fluorescence ratio recorded at 460 and 500 nm. The total times of irradiation were obtained using either one single flash, or a series of flashes.

Fig. 6 The influence of the length of the pause on the final ratio of the fluorescence intensities recorded at 460 and 500 nm. Photopolymerization of a TMPTMA-VP (9:1) mixture: Poly-RBAX ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), various LRSs, 15 flashes, total time of irradiation 3 sec., 600 mW/1.54 mm^2, 514 nm.

Fig. 7 The influence of the length of the pause on the final degree of double bond conversion observed during the photopolymerization of a TMPTMA-VP mixture: Poly-RBAX ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), various LRSs, 15 flashes, total time of irradiation 9 sec., 800 mW/5 cm^2, 514 nm.

Fig. 8 The influence of post irradiation processes on the probe fluorescence ratio recorded at 460 and 500 nm. Photopolymerization of a TMPTMA-VP mixture: PolyRBAX ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), 5 sec. single flash, 600 mW/1.54 mm^2, 514 nm.

Fig.9 TFTIR measurements of the long-term dark polymerization of a TMPTMA-VP mixture: Poly-RBAX ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l) total time of irradiation 9 sec., 800 mW/5 cm^2, 514 nm

Fig. 10 The effect of light intensity on the initial rate of polymerization. Polymerization of a thick sample of a TMPTA-VP mixture: Poly-RBAX ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), 100 ms single flash, 514 nm.

Fig. 11 The changes of dansyl amide fluorescence recorded during and after polymerization of a TMPTMA-VP mixture: Poly-RBOH ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), LRS (0.2-10-...), 15 flashes, total time of irradiation 3 sec., 600 mW/1.54 mm^2, 514 nm.

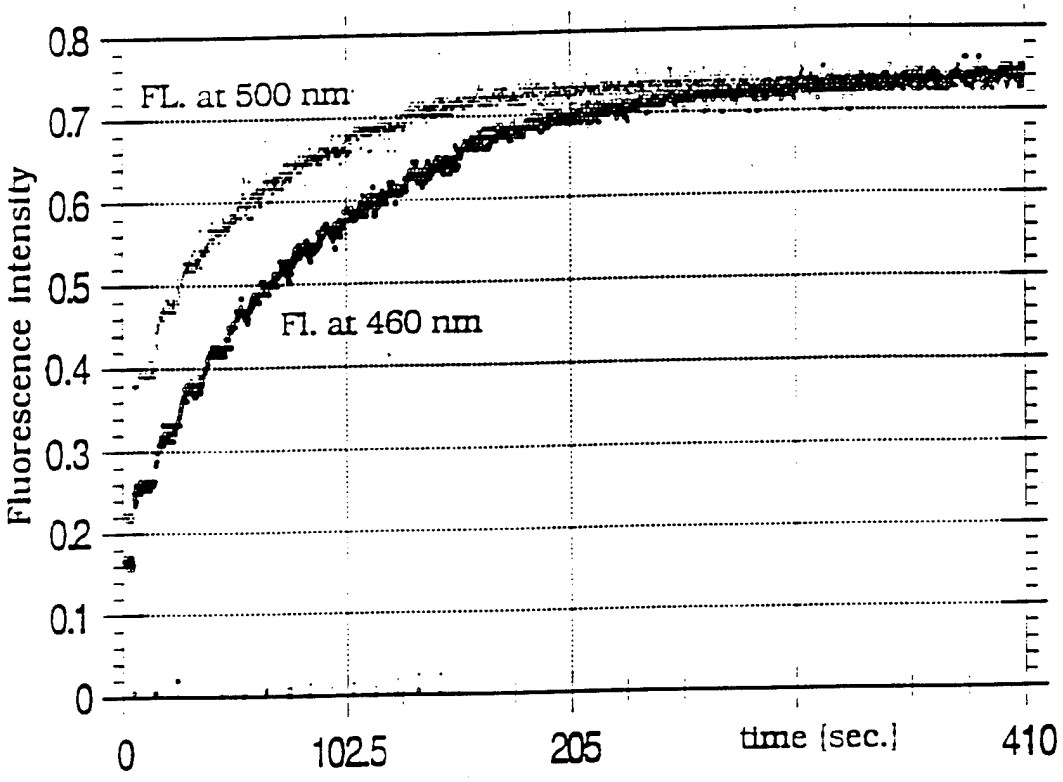
Fig. 12The change of dansyl amide fluorescence recorded during and after polymerization of a TMPTMA-VP (9:1) mixture:
a) Poly-RB-OAc ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), LRS (0.2-0.2-....) 15 flashes, total time of irradiation 3 sec, 600 mW/1.54 mm^2, 514 nm.
b) Poly-RB-OAc ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), LRS (0.2-10-...), 15 flashes, total time of irradiation 3 sec. 600 mW/1.54 mm^2, 514 nm.

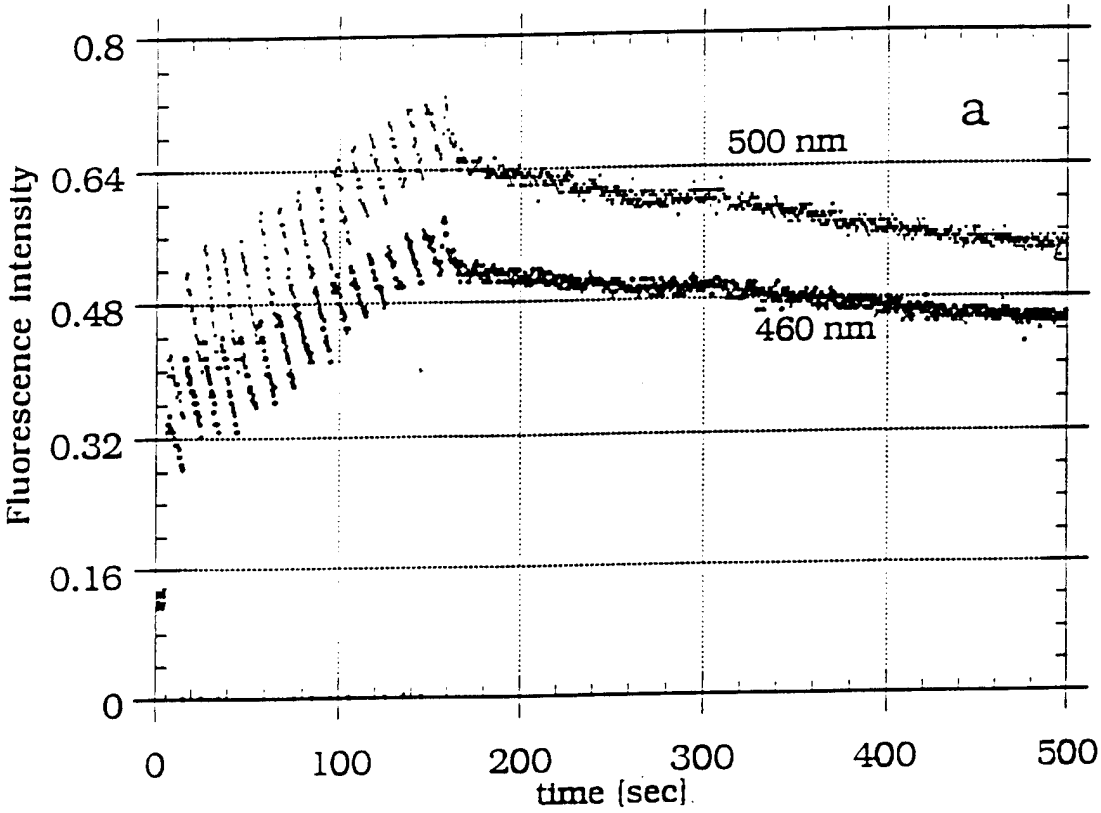
Fig. 13 The influence of the duration of the pause between irradiation flashes on the final ratio of dansyl amide fluorescence intensities recorded at 460 and 500 nm. Photopolymerization of a TMPTMA-VP mixture: Polt-RB-OAc ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), various LRSs, total time of irradiation 3 sec., 600 mW/1.54 mm^2, 514 nm.

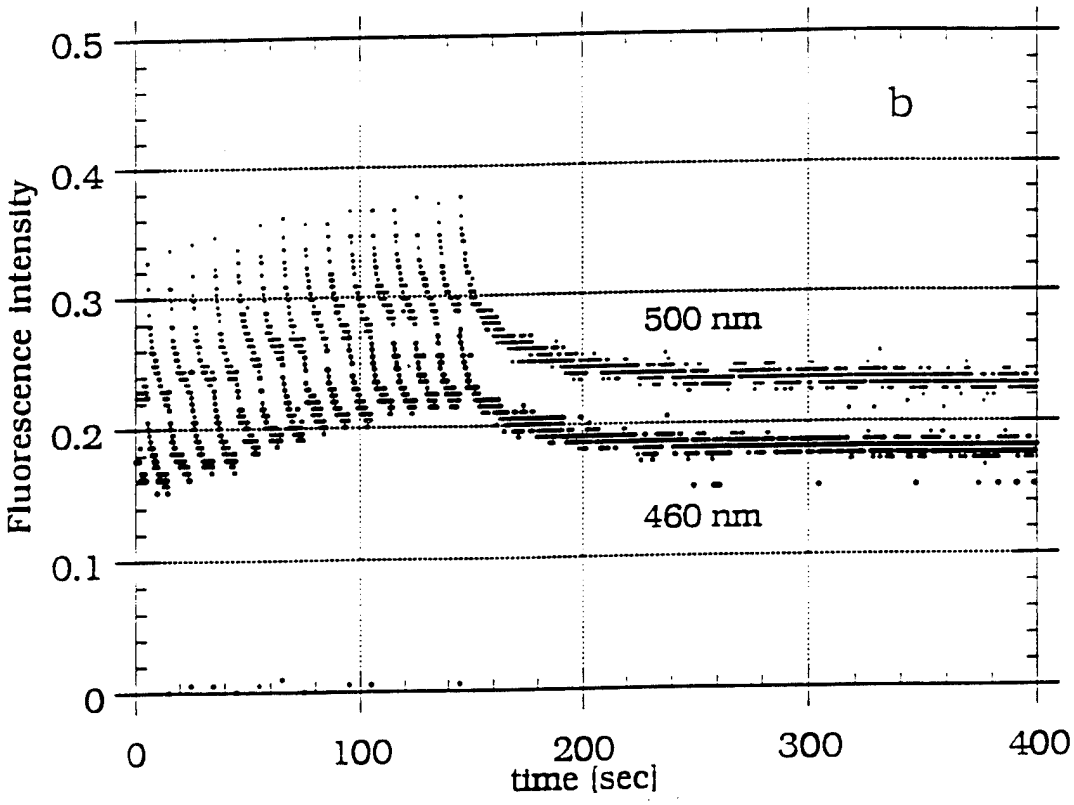
Fig. 14 The influence of the duration of the pause between irradiation flashes on the final degree of double bond conversion measured using FTIR (at 810 cm^{-1}). Photopolymerization of a TMPTMA-VP mixture: Poly-RB-OAc ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), various LRSs, 15 flashes, total time of irradiation 9 sec., 800 mW/2.5 cm^2, 514 nm.

Fig. 15 The long-term post-irradiation polymerization of a TMPTMA-VP mixture: Poly-RB-OAc ($5x10^{-4}$ mol/l of RB molecules), NPG (0.05 mol/l), total time of irradiation 9 sec., 800 mW/2.5 cm^2, 514 nm.

Fig 1


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Fluorescence Intensity
FL. at 500 nm
Fl. at 460 nm
0
102.5
205
time (sec.)
410


0.8
0.64
0.48
0.32
0.16
0
Fluorescence Intensity
a
500 nm
460 nm
0
100
200
300
400
500
time (sec)


0.5
0.4
0.3
0.2
0.1
0
Fluorescence Intensity
b
500 nm
460 nm
0
100
200
300
400
time [sec]

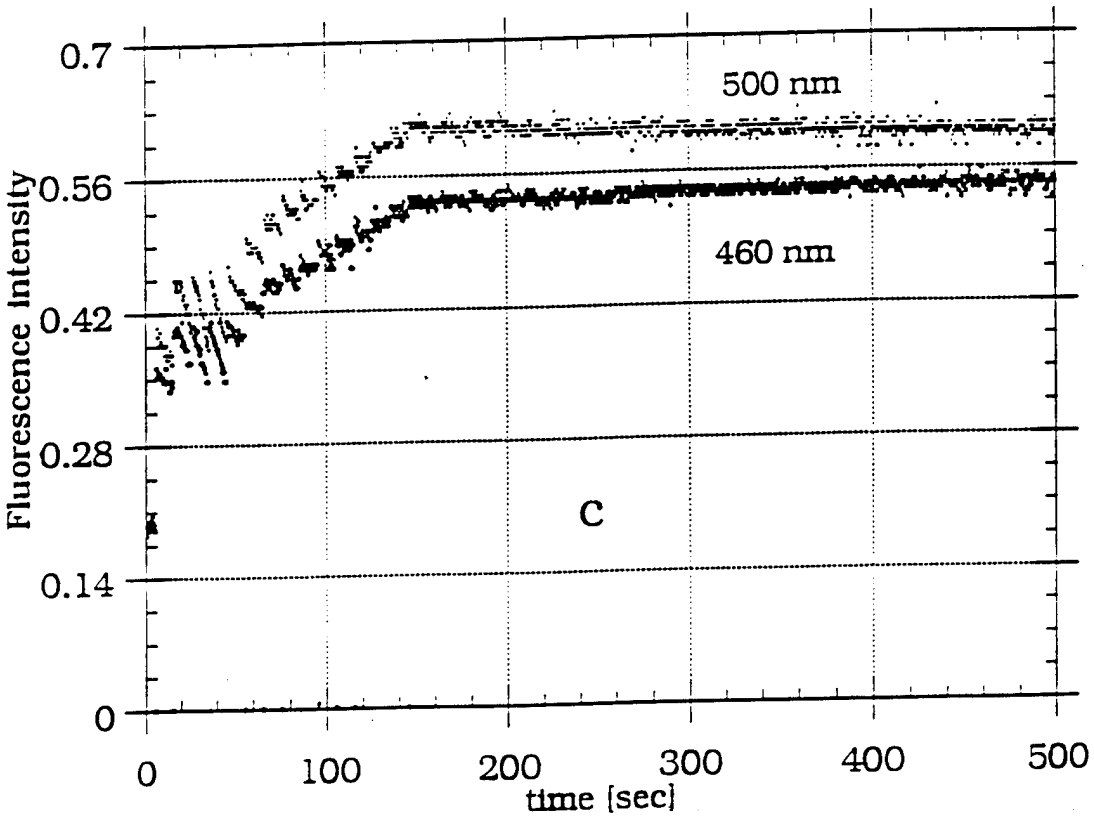
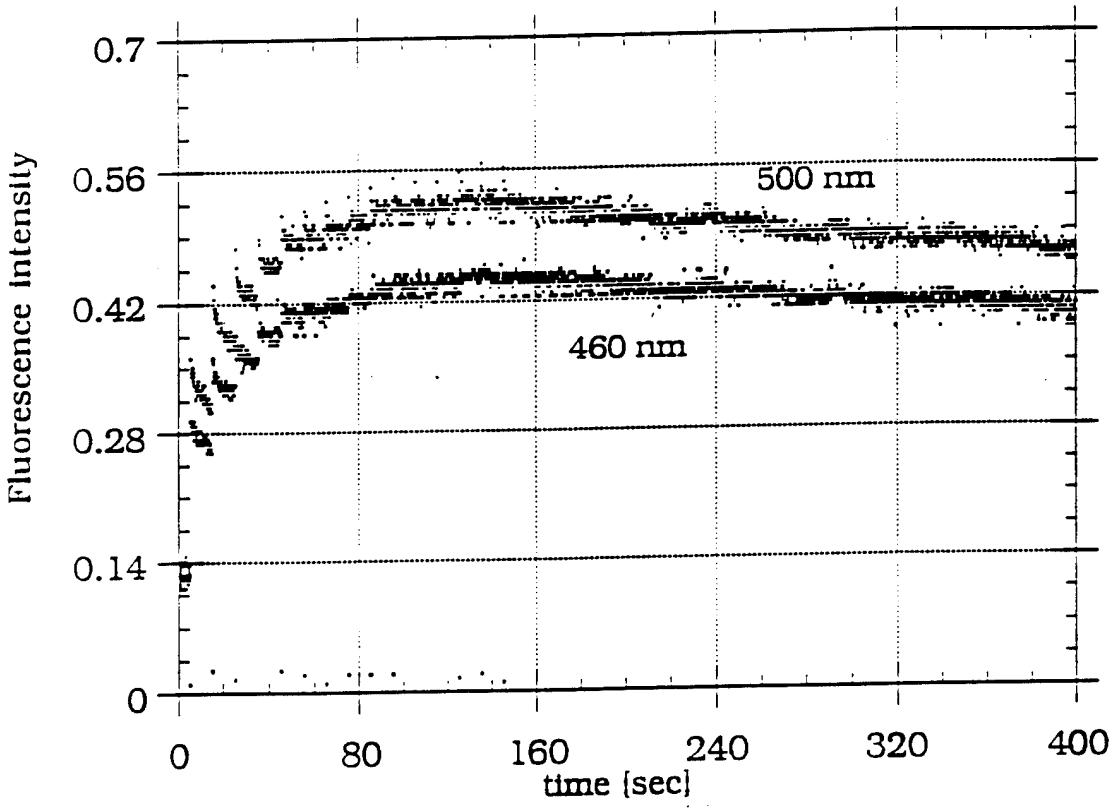
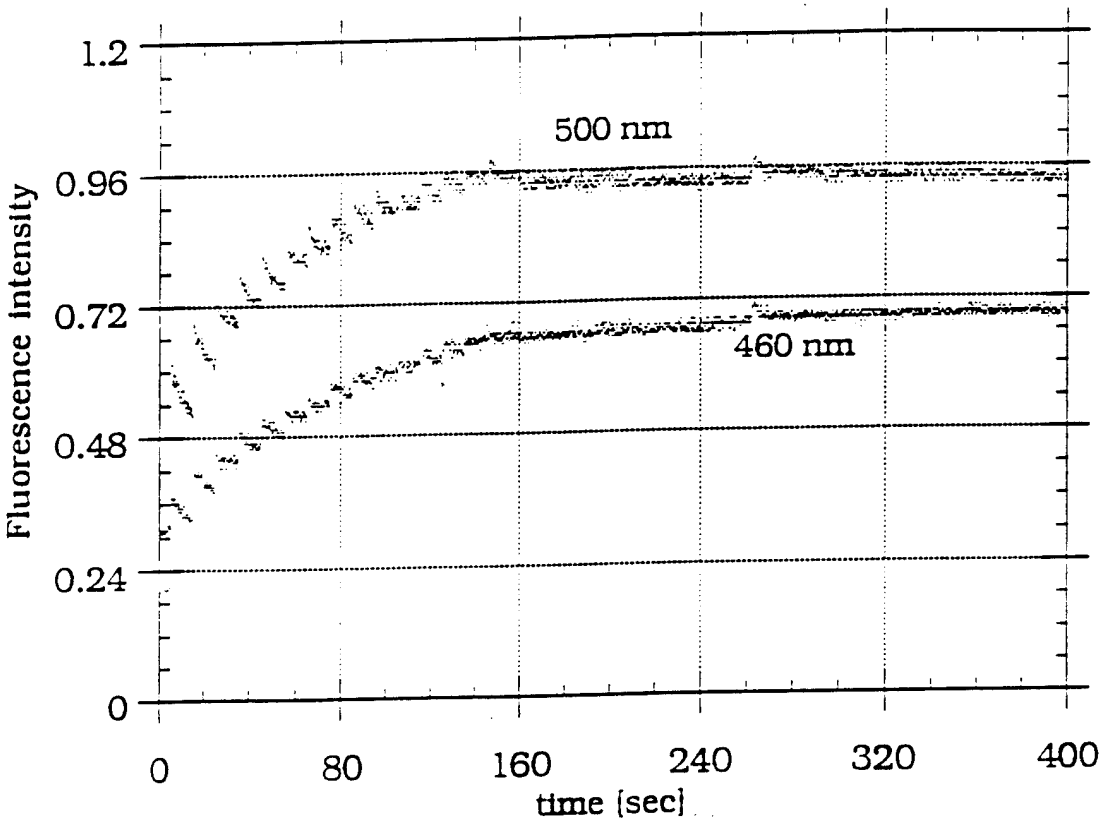
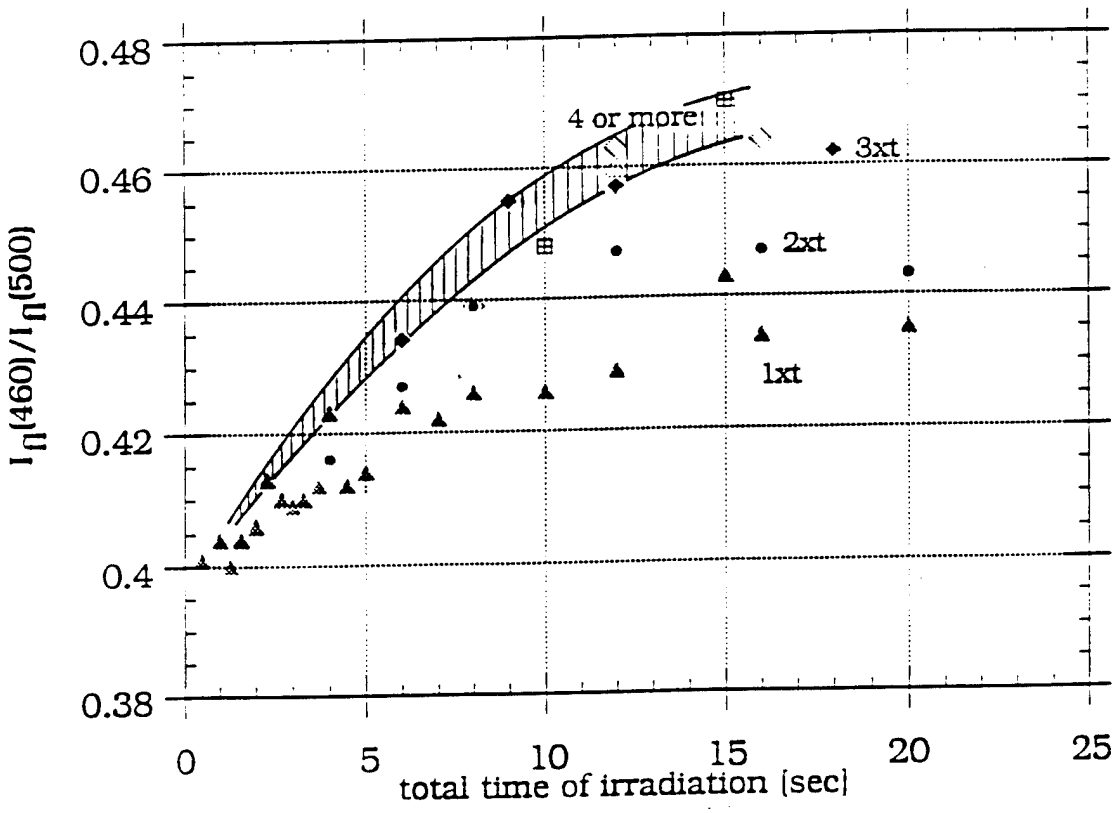
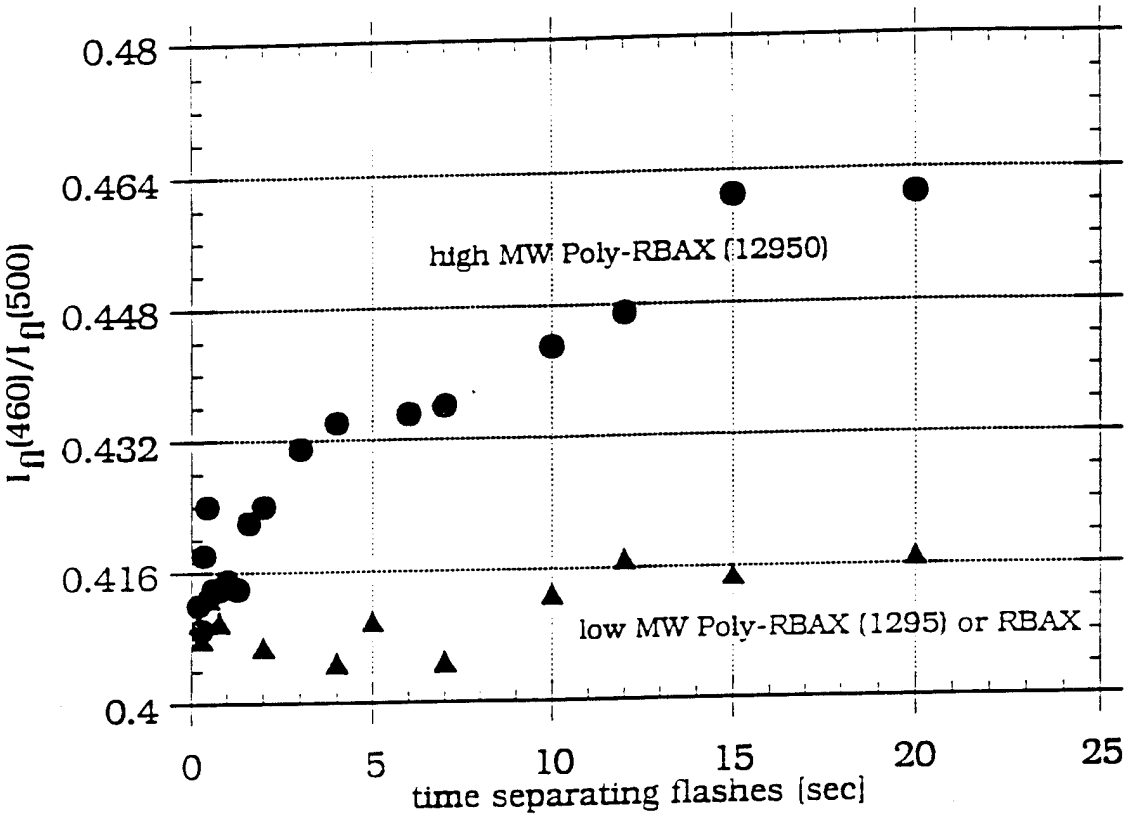

0.7
0.56
0.42
0.28
0.14
0
Fluorescence Intensity
500 nm
460 nm
C
0
100
200
300
400
500
time [sec]

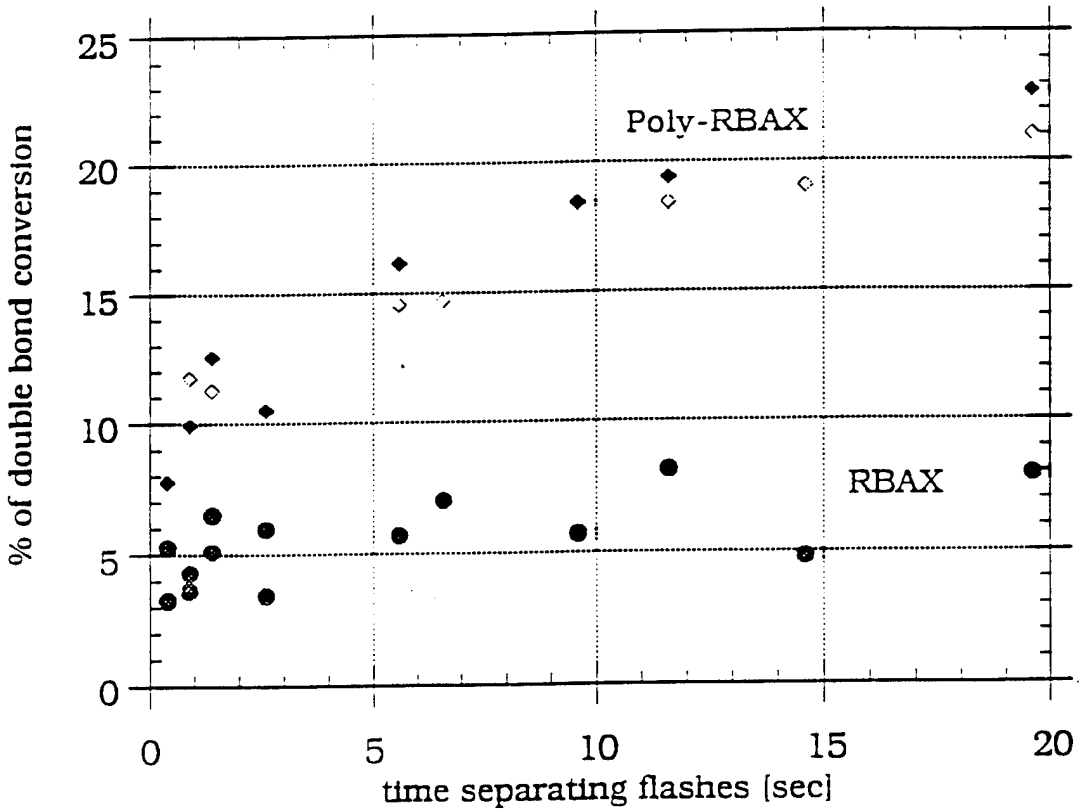
Fig. 3

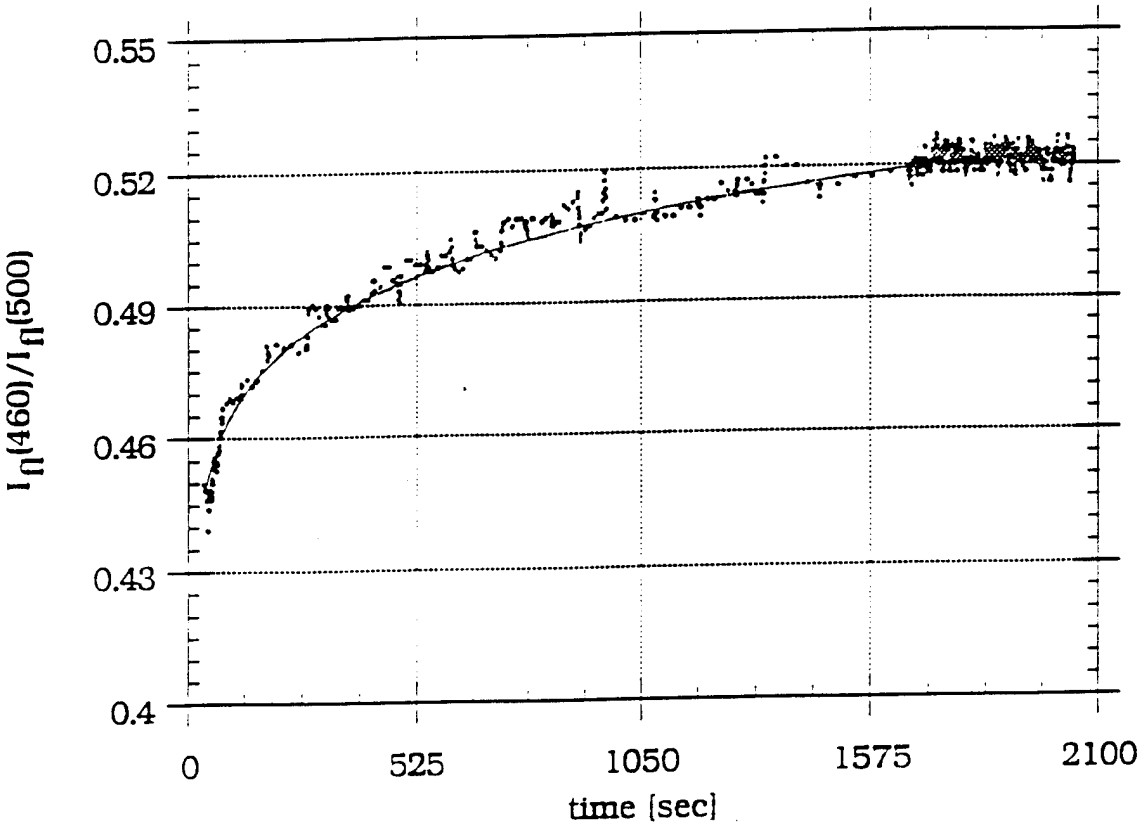

0.7
0.56
0.42
0.28
0.14
0
Fluorescence Intensity
500 nm
460 nm
0
80
160
240
320
400
time [sec]

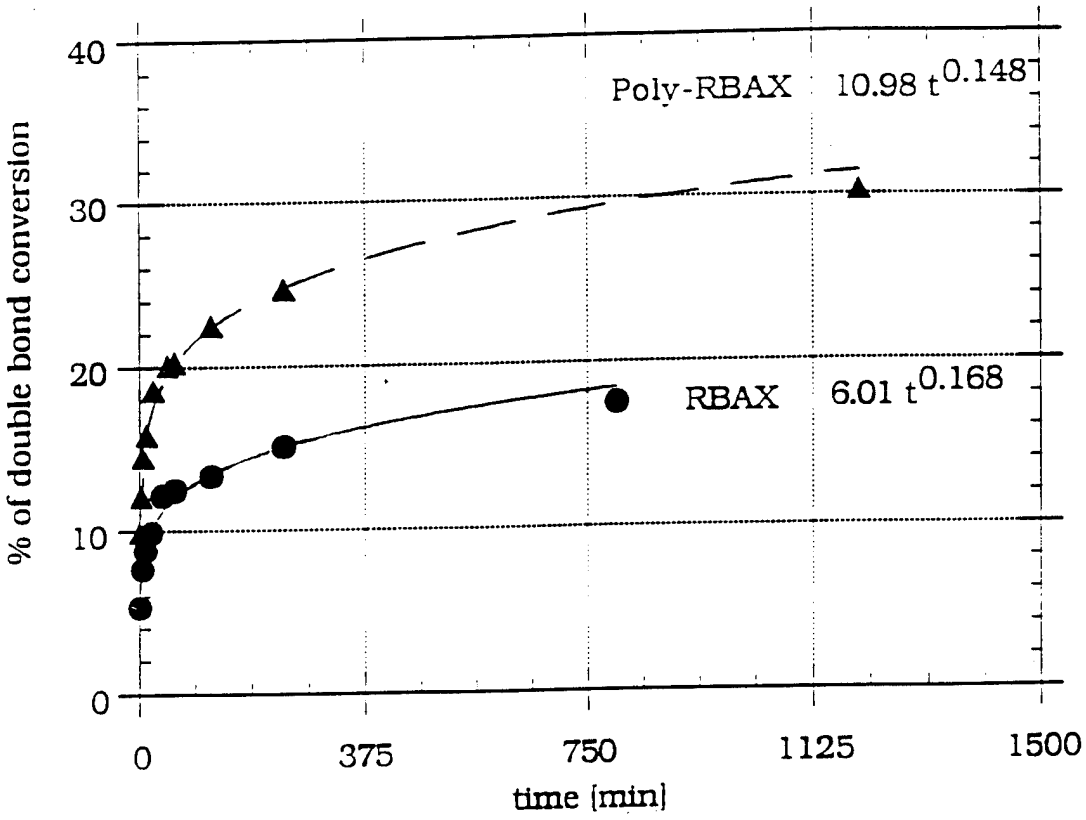

1.2
0.96
0.72
0.48
0.24
0
Fluorescence intensity
500 nm
460 nm
0
80
160
240
320
400
time [sec]

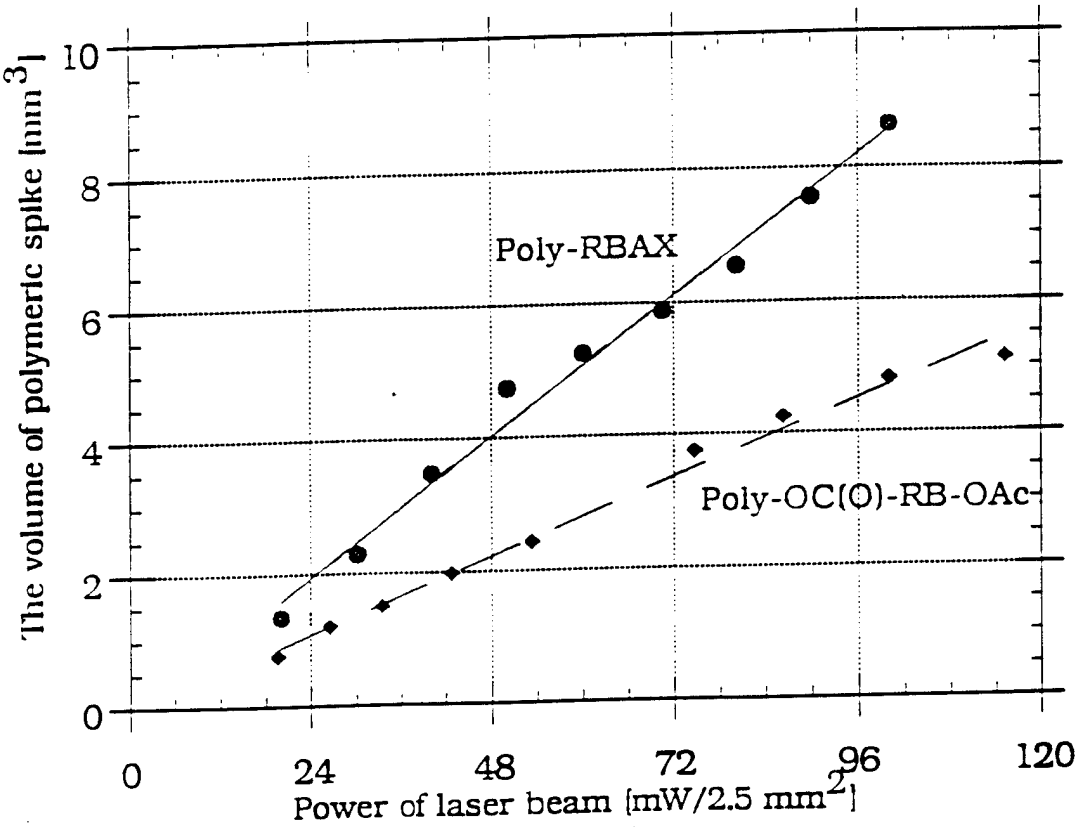

0.48
0.46
0.44
0.42
0.4
0.38
0
5
10
15
20
25
$I_{\Pi}(460)/I_{\Pi}(500)$
total time of irradiation [sec]
4 or more
3xt
2xt
1xt

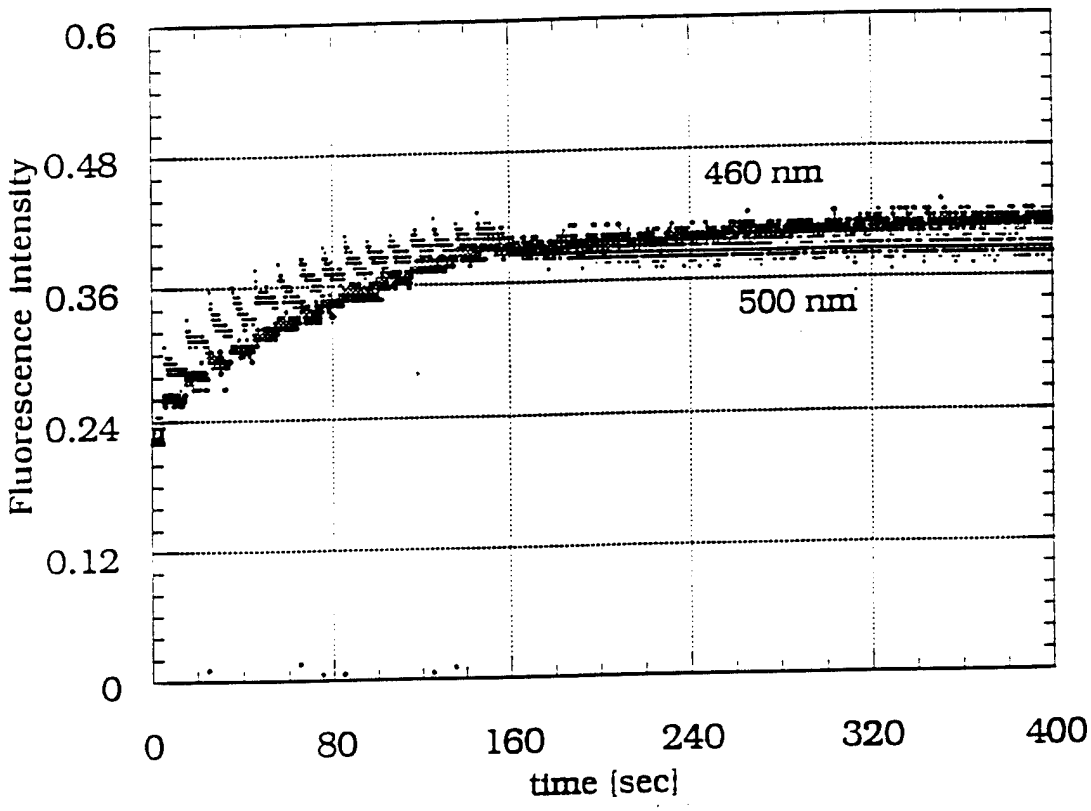

0.48
0.464
0.448
0.432
0.416
0.4
$I_{fl}(460)/I_{fl}(500)$
high MW Poly-RBAX (12950)
low MW Poly-RBAX (1295) or RBAX
0
5
10
15
20
25
time separating flashes [sec]

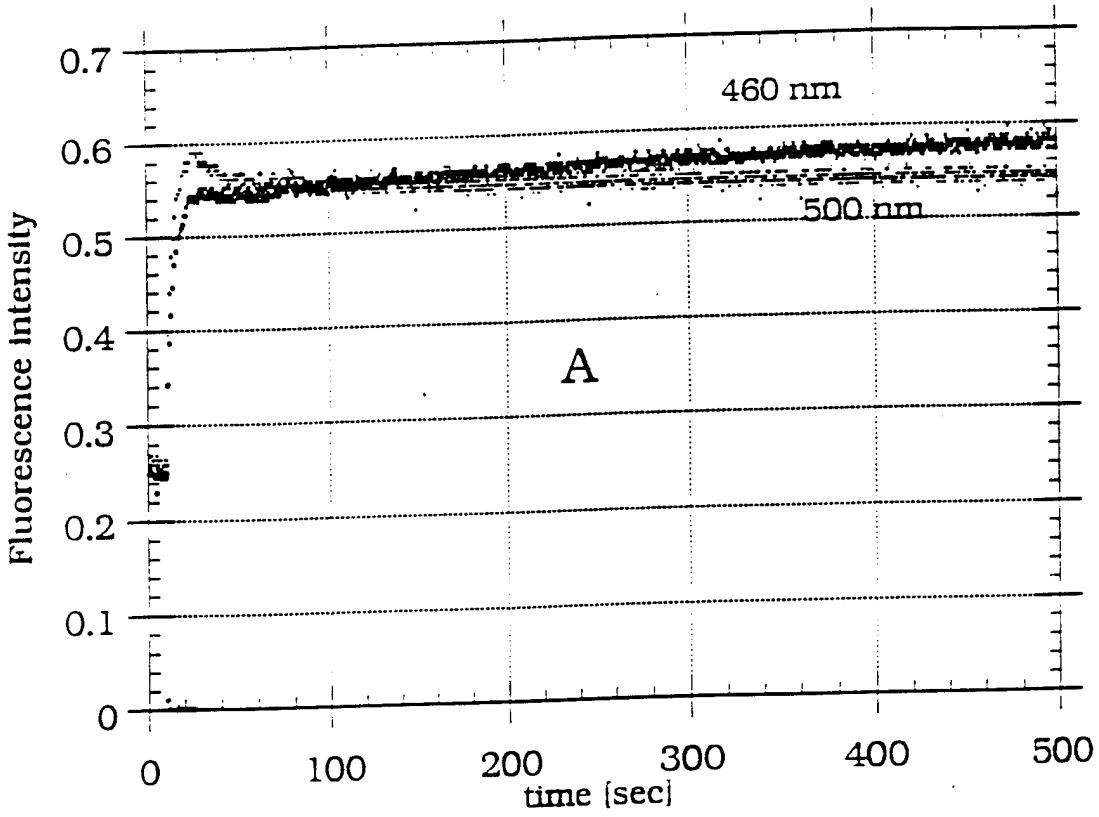

25
20
15
10
5
0
% of double bond conversion
Poly-RBAX
RBAX
0
5
10
15
20
time separating flashes [sec]

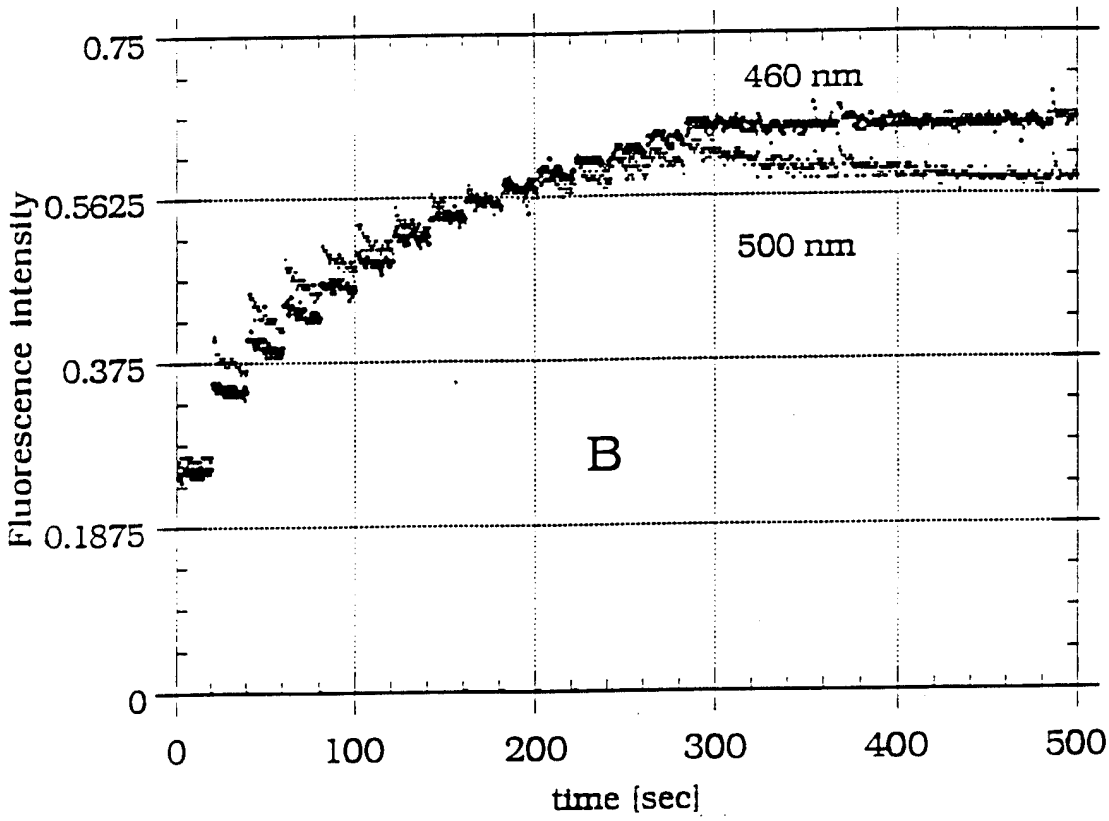

0.55
0.52
0.49
0.46
0.43
0.4
$I_{\Pi}(460)/I_{\Pi}(500)$
0
525
1050
1575
2100
time [sec]

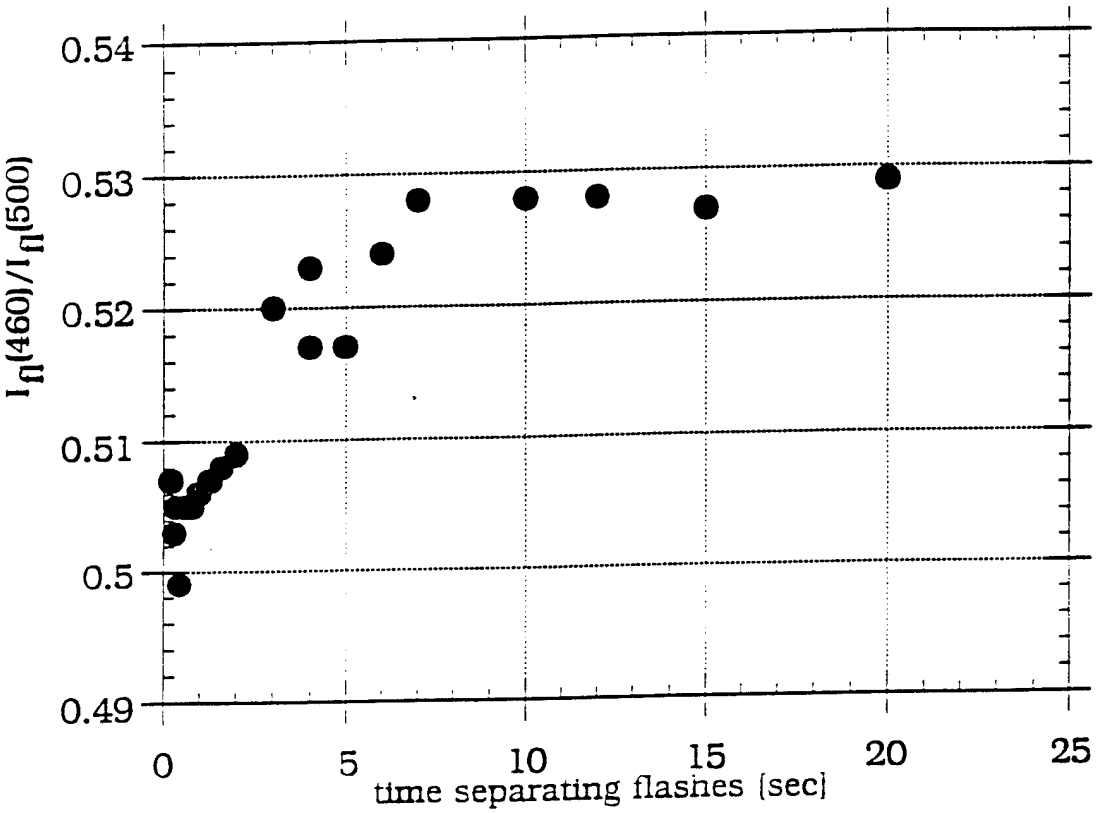

40
30
20
10
0
% of double bond conversion
Poly-RBAX 10.98 t^0.1487
RBAX 6.01 t^0.168
0
375
750
1125
1500
time [min]

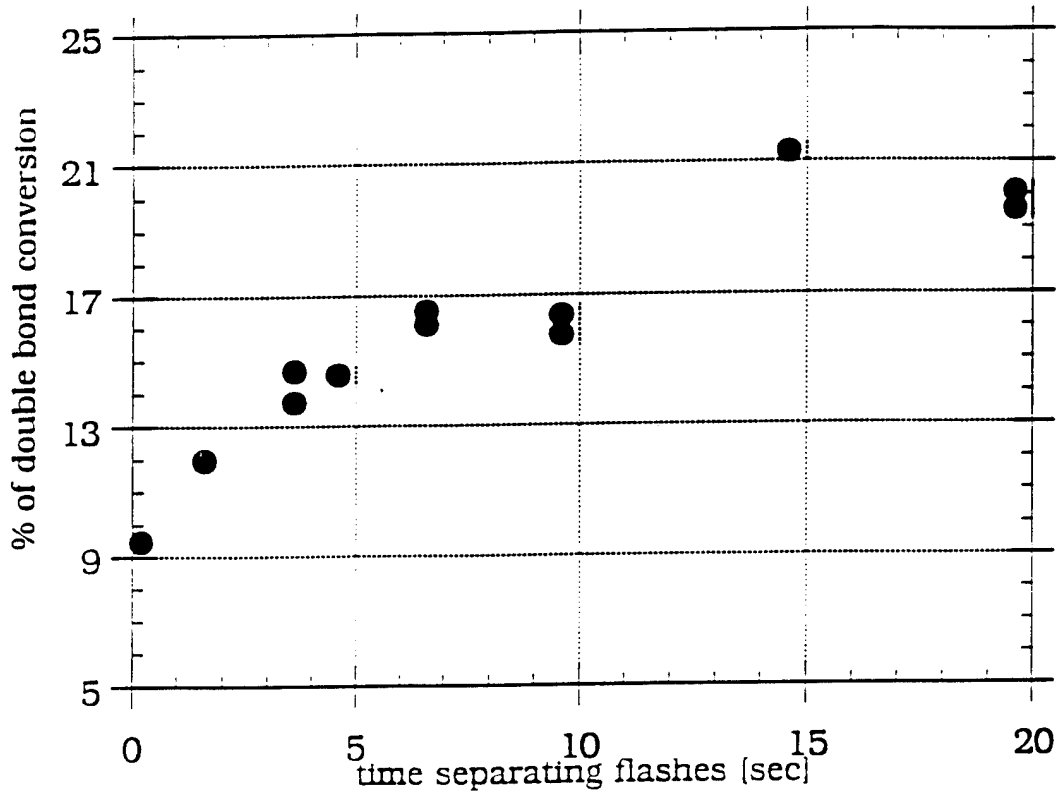

The volume of polymeric spike [mm^3]
10
8
6
4
2
0
Poly-RBAX
Poly-OC(O)-RB-OAc
0
24
48
72
96
120
Power of laser beam [mW/2.5 mm^2]

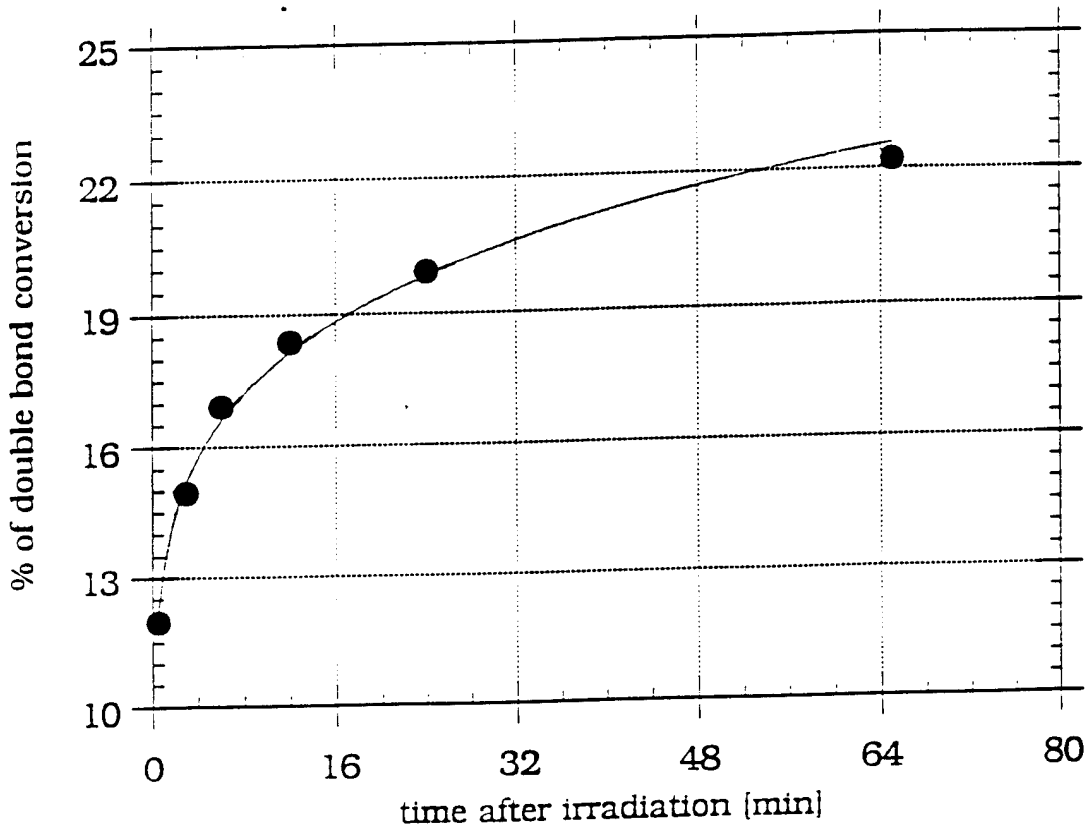

0.6
0.48
0.36
0.24
0.12
0
Fluorescence Intensity
460 nm
500 nm
0
80
160
240
320
400
time [sec]


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Fluorescence Intensity
460 nm
500 nm
A
0
100
200
300
400
500
time [sec]

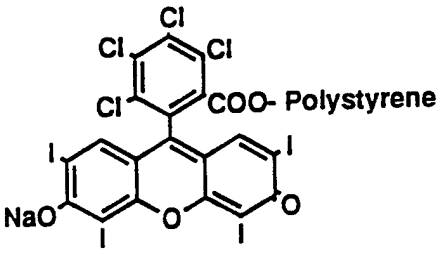

0.75
0.5625
0.375
0.1875
0
Fluorescence Intensity
460 nm
500 nm
B
0
100
200
300
400
500
time [sec]


0.54
0.53
0.52
0.51
0.5
0.49
$I_{fl}(460)/I_{fl}(500)$
0
5
10
15
20
25
time separating flashes (sec)

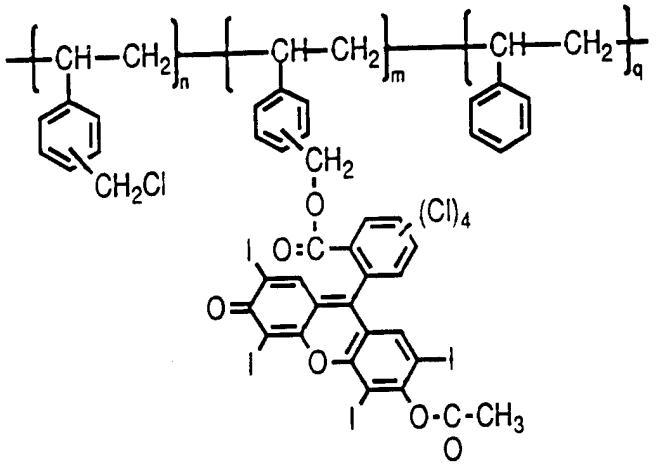

25
21
17
13
9
5
% of double bond conversion
0
5
10
15
20
time separating flashes [sec]


25
22
19
16
13
10
% of double bond conversion
0
16
32
48
64
80
time after irradiation [min]

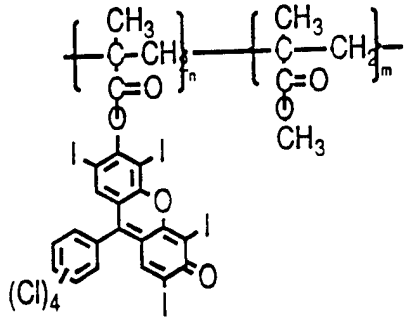
Scheme I



Polymer Rose Bengal



Poly-RBOAc;



Poly -RBAX